Spectra calculations in central and wing regions of CO₂ IR bands between 10 and 20 μm. III: atmospheric emission spectra

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Abstract

A theoretical model for the prediction of CO₂ absorption in both central and wing regions of infrared absorption bands was presented in the companion paper I. It correctly accounts for line-mixing effects and was validated by comparisons with laboratory spectra in the 600–1000 cm⁻¹ region. This quality was confirmed using atmospheric transmissions measured by solar occultation experiments in the second paper. The present work completes these studies by now considering atmospheric emission in the 10–20 μm range. Comparisons are made between computed atmospheric radiances and measurements obtained using four different Fourier transform experiments collecting spectra for nadir, up-looking, as well as limb (from balloon and satellite) geometries. Our results confirm that using a Voigt model can lead to very large errors that affect the spectrum more than 300 cm⁻¹ away from the center of the CO₂ v₂ band. They also demonstrate the capability of our model to represent accurately the radiances in the entire region for a variety of atmospheric paths. This success opens interesting perspectives for the sounding of pressure and temperature profiles, particularly at low altitudes. Another benefit of the quality of the model should be an increased accuracy in the retrieval of atmospheric state parameters from broad features in the measured spectra (clouds, aerosols, heavy trace gases).

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1. Introduction

The need for correct forward modeling of CO₂ absorption for the treatment of atmospheric spectra is now well known and large efforts have been devoted to this subject (see Refs. [1–3] and those cited there in). Whereas precise models have been proposed for isolated transitions and Q branches [3,4], the line and band wings have received a much poorer treatment based on empirical line-shape correction factors $\chi$. These are approximate, have very little physical basis, and, due to lack of data, the wings of the $\Pi \leftarrow \Sigma v_2$ band have to be computed using values of $\chi$ determined in the $\Sigma \leftarrow \Sigma v_3$ band. This situation, which has led to discrepancies between measured and calculated atmospheric spectra in the 15 μm region (e.g. [5]), also called for a precise and unified approach permitting the treatment of all CO₂ absorption features, including local transitions, dense Q branches, and the line wings.

Such a model was proposed in a preceding companion paper [1]. It uses the energy corrected sudden approximation in order to construct the line-mixing relaxation matrix. It correctly and automatically accounts for the symmetry of the vibrational levels and for the coupling of angular momenta thus permitting calculation of line-coupling between any (P, Q, and R) lines within any band. Comparisons between predictions of this model and temperature-dependent laboratory measurements for CO₂–N₂ mixtures [1] in the 15 μm region have demonstrated the quality of this approach. The shape of the central part of the intense bands at elevated pressure is well described and absorption in the wings is satisfactorily modeled in a wide range of wavenumbers around the band centers. Further tests of this approach have been made in Ref. [2] by comparisons between forward calculations and atmospheric transmissions measured using balloon-borne and ground-based solar occultation experiments. They have confirmed the quality of the model and the importance of errors induced by the use of purely Voigt line shapes. Furthermore recall that, as explained in [1], the present model is an extension of that initially developed for Q branches [3,6] whose quality was widely demonstrated using laboratory and atmospheric measurements.

The present paper extends the test of the model by making comparisons between forward calculations and atmospheric radiances measured by different Fourier transform instruments. A number of emission spectra are used which correspond to various geometries including nadir, up-looking, and (balloon and satellite borne) limb viewings. The results confirm the quality of the approach proposed with which all measurements are correctly reproduced. In particular, whereas use of the Voigt model can lead to very large errors, deviations between measurements and our calculations show no specific broad features over the entire spectral ranges studied. Among various remote sensing possibilities offered by the quality of the model, that of retrieving species that make small contributions highly contaminated by CO₂ emission is demonstrated.

2. Atmospheric spectra

The atmospheric emission spectra used have been recorded by four different Fourier transform instruments that have all been carefully calibrated and provide absolute radiances.

The high-resolution interferometer sounder (HIS) [7] was developed by the University of Wisconsin to measure thermal radiation emitted by the atmosphere. It is a Fourier transform instrument with a spectral resolution of about 0.3 cm⁻¹ (unapodized). The radiance spectra used in the present
work cover the 600–850 cm\(^{-1}\) range and have been collected on 14 April 1986 and 31 October 1988. The first spectrum was recorded in nadir viewing from NASA ER-2 aircraft (20 km altitude) during test flight off the California Coast (120°W, 35°N). The second was recorded from ground in Colorado (105°W, 40°N), looking up.

In the Smithsonian Astrophysical Observatory (SAO) experiment [8] a balloon-borne Fourier transform instrument (FIRS-2, 0.004 cm\(^{-1}\) resolution unapodized) is used. The limb viewing spectra analyzed in the present work were obtained on 30 April 1997 over Alaska (150°W, 68°N). They consist of nine radiance spectra in the 500–850 cm\(^{-1}\) spectral range recorded at N[—oat (balloon at 40 km) for tangent heights from about 37km down to 10 km.

In the Michelson interferometer for passive atmospheric sounding (MIPAS) experiment [9], a satellite (ENVISAT) borne FTIR (0.035 cm\(^{-1}\) resolution unapodized) is used. The limb viewing measurements analyzed in the present work were obtained on 24 July 2002. They consist of 15 radiance spectra in the 690–970 cm\(^{-1}\) spectral range recorded from the altitude of 786 km on a 22°W longitude polar orbit. The lines of sight have tangent points with altitudes between 8 and 70 km at the location 22°W and 42–45°N. These spectra were recorded during the commissioning phase of MIPAS and were released by the European Space Agency (ESA) for testing and calibration/validation purposes only. While they have not been generated with the most advanced processor setup, these early data proved to be a valuable reference for radiative transfer model validation.

3. Theoretical model

The quantities deduced from the atmospheric experiments used in the present work are radiances \(I\). Given a model for the calculation of the absorption coefficient, neglecting diffusion and latitudinal and longitudinal inhomogeneities, their values at wavenumber \(\sigma\) are given by

\[
I(\sigma) = \int_{\text{FOV}} d\Omega \int_{-\infty}^{+\infty} F_{\text{Instr}}(\sigma - \sigma') \times [I_{\text{Atm}}(\sigma', d\Omega) + t_{\text{Atm}}(\sigma', d\Omega) \times I_{\text{End}}(\sigma', d\Omega)] d\sigma'.
\]

For a given spectrum, integration is made over the field of view (FOV) of the instrument and radiances are convolved by the normalized instrument function \(F_{\text{Instr}}\). \(I_{\text{Atm}}\) and \(I_{\text{End}}\) are spectral values of the intensity emitted by the atmosphere and that radiated, towards the observer, at the end of the optical path, and \(t_{\text{Atm}}\) is the spectral transmission of the optical path. Note that \(I_{\text{End}}(=I_{\text{Ground}})\) is due to surface emission for nadir viewing and, in the absence of clouds, \(I_{\text{End}}\) is zero for experiments collecting radiances at limb and up-looking. For strongly absorbing grounds, reflected radiation is negligible and \(I_{\text{End}}\) only depends on the surface emissivity and temperature. Assuming local thermodynamic equilibrium (LTE), the spectral emission and transmission of the atmosphere are given by

\[
t_{\text{Atm}}(\sigma, d\Omega) = \exp \left\{ -\sum_a \int_{Z_{\text{obs}}}^{Z_{\text{end}}} \alpha_a[\sigma, x_a(z), P(z), T(z)] \frac{ds}{dz} (z, d\Omega) dz \right\},
\]

\[
I_{\text{Atm}}(\sigma, d\Omega) = \int_{Z_{\text{obs}}}^{Z_{\text{end}}} \left\{ \sum_a \alpha_a[\sigma, x_a(z'), P(z'), T(z')] \times I_0[\sigma, T(z')] \times \exp \left\{ -\sum_a \int_{Z_{\text{obs}}}^{Z'} \alpha_a[\sigma, x_a(z), P(z), T(z)] \frac{ds}{dz} (z, d\Omega) dz \right\} \frac{ds}{dz} (z', d\Omega) dz' \right\},
\]
where $I_0$ is the black body radiance. For each optical path an integration is carried out from the observation point at altitude $z_{\text{Obs}}$ to the end of the path at altitude $z_{\text{End}} (= z_{\text{Ground}}$ for nadir, and $= z_{\infty}$ for the other geometries) following the curvilinear abscissa $s$ along the considered line of sight. The sum extends over all species “$a$” that make significant contributions to the spectrum in the considered spectral range through their spectral absorption coefficient $x_a$, the total pressure, and the temperature, respectively. As mentioned above, the preceding equations assume LTE since all quantities are evaluated using the kinetic temperature. This approximation breaks down at elevated altitude where intermolecular collisions are too few for vibrational relaxation to maintain equilibrium. For most species, including CO$_2$, effects are significant above 50 km or higher and they have negligible consequences on the spectra analyzed in the following since they involve significantly lower tangent altitudes [10,11].

In the present work, only absorption by molecules is accounted for while contributions of aerosols and clouds are disregarded since they are absent in the considered measurements.\(^1\) The absorption coefficients of the various species that contribute to atmospheric absorption in the spectral region of interest have been computed with the models described in Section 3 of Ref. [2]. Recall that, for CO$_2$, calculations accounting for line-mixing using the model of Ref. [1] are made together with predictions based on the addition of Voigt contributions (no line-mixing).

4. Data used and computational details

The spectroscopic data used in the calculations are the same as those described in Section 4 of [2] where all information can be found.

The instrument function of the HIS experiments is that of a Michelson interferometer with a 1.37 cm maximum optical path difference leading to a resolution of about 0.36 cm$^{-1}$ as explained in Ref. [7]. The FIRS-2 maximum optical path difference is 125 cm, leading to a resolution of 0.004 cm$^{-1}$. For MIPAS, a pretabulated ILS has been used which takes into consideration some instrument-specific deviations from the ideal ILS of a Michelson Fourier transform spectrometer.

For the simulation of the balloon- and satellite-borne emission spectra, the geometry of the optical path was deduced from the observation elevation angle and a ray tracing procedure. The pointing in the SAO measurements is obtained from a stabilized inertial reference platform on the instrument which is good to 0.02°. Fine corrections are obtained by adjusting the angles through ray tracing and radiative transfer to get correct column amounts along the line of site for both CO$_2$ and O$_2$. In the case of MIPAS spectra, recent studies [12] have indicated that the pointing information given by the instrument system is uncertain. While relative variations of the elevation angle between adjacent tangent altitudes are relatively well known, there are large uncertainties with respect to the absolute elevation angle, which lead to tangent height errors of up to 3 km. Hence, we have used here elevation angle corrections retrieved [12] along with the temperature profile directly from the CO$_2$ emissions from various transitions.

\(^1\)This will be shown by the absence of any underlying broad structure in the measured-calculated differences presented in the following. In the case of the MIPAS recordings used here, this is confirmed by an analysis, made by the Service d’Archivage et de Traitement Météorologique des Observations Spatiales (Météo France), of infrared and visible data from the advanced very high-resolution radiometer (National Oceanic and Atmospheric Administration) and Meteosat (Eumetsat) for the times, altitudes, latitudes and longitudes of the limb spectra used in the present work.
Fig. 1. HIS radiance collected at nadir from the altitude of 20 km. The upper part gives measured values and the curves in lower part are measured-calculated deviations obtained with (a) and without (b) inclusion of line mixing. (c) and (d) have been obtained from (a) and (b) by averaging over 1 cm$^{-1}$.

Fig. 2. Residuals between measured values and the results of calculations with our model normalized by the uncertainty on the measurements: (a) raw results, (b) after averaging over 1 cm$^{-1}$.
The temperature and total pressure vertical profiles for the HIS spectra were obtained from combined use of soundings and meteorological data. For the SAO experiments [8], a combination of local sonde data and radiance corrections is used to get temperature and pressure information. Micro-windows in the CO\(_2\) band where the radiance is saturated at specific altitudes along the line of site are chosen and radiative transfer calculations are performed to correct the temperature from that determined by the local sonde data. For MIPAS, temperatures are retrieved as a by-product of the elevation angle (tangent altitude) retrieval [12]. For these temperatures and altitudes a hydrostatic pressure profile is then built up.

The species which provide the principal absorption lines in the spectral regions under study are CO\(_2\), O\(_3\), HNO\(_3\), CFC-11 and CFC-12. Some minor or local contributions come from H\(_2\)O, ClONO\(_2\), CCl\(_4\), and further. For the simulation of each experiments, the CO\(_2\) amount was set to the nominal value for the year of observation. For the HIS measurements, the vertical profiles of O\(_3\) and H\(_2\)O were those retrieved by the HIS group, all other (minor) constituents being set to climatological mean found in the AFGL U.S. Standard Atmosphere. Forward calculations of the FIRS-2 spectra were made using vertical profiles deduced by the SAO group [8] from fit of the spectra, starting with known profiles from past data sets. In the case of MIPAS, profiles of constituents were taken from a dedicated database containing climatological profiles [13].
Fig. 4. MIPAS radiance collected from 790 km for a tangent height of 34.5 km. The upper part gives measured values and the curves in lower part are measured-calculated deviations obtained with (a) and without (b) inclusion of line mixing.

Fig. 5. Detailed view of the results of Fig. 4 in the region of the \((v_1 - v_2)\) Q branch: • measured values; — computation accounting for line-mixing; - - - - computation neglecting for line-mixing. Residuals (obs-calc) are given in the lower part.
Computations have been made with the procedures described in Ref. [2] except for the integration over the FOV which was disregarded in our previous work. Indeed, in the MIPAS measurements, the high altitude of the instrument leads to a distance between the instrument and the tangent point of about 3000 km. Although small, the MIPAS FOV corresponds a vertical extent of about 3 km at the tangent point and neglecting it can lead to significant errors [14]. Indeed, at low altitudes the emission in the CO$_2$ wings grows quickly due to the increase of pressure and temperature, and the radiances along different rays within the FOV are quite different. Hence, the integration over the elevation FOV was performed while carrying out forward calculations to be compared with the MIPAS measurements. In order to do this, radiances along six lines of sight within the vertical FOV were calculated and integrated using a pretabulated response function as determined in laboratory measurements.

5. Results and discussion

Comparisons between measured and computed values of radiances for various viewing geometries are presented below. Note that all forward calculations are made without use of any adjustable
parameter and that measured spectra have received no correction. In all cases, calculations for CO$_2$
are made with our model, with and without ($Y'_f = 0$, purely Voigt line shapes) the inclusion of
line-mixing. The results of Refs. [1,2] show that this phenomenon leads to a strong lowering of
absorption in the wings. As analyzed in Ref. [3], it can lead to the increase or decrease of atmospheric
radiances, depending on the variations of local absorption and emission along the optical path.

Fig. 1 presents a comparison between HIS measured and calculated radiances for the case of a
nadir viewing. It shows that the use of Voigt profiles (neglecting line mixing) leads to large errors
that extend over the entire spectral range. The strong overestimation of the v$_2$ wings predicted by this
model [1] leads to underestimated radiances, mostly through the underestimation of the transmission,
by the atmosphere, of the ground emission. On the contrary, our model leads to very satisfactory
results. Most discrepancies are due to small frequency shifts, noise, or very localized improper
spectroscopic data as indicated by the 1 cm$^{-1}$ averaged values. In particular, deviations are “flat"
and show no underlying structure, contrary to what was observed in comparisons with a number of
models [5]. Indeed, radiance residuals, normalized by the uncertainty of measurements, plotted in
Fig. 8. Same as Fig. 7 but for a tangent height of 8.4 km.

Fig. 9. Detailed view of the results of Fig. 8 in the region of the R(31)–R(41) line of the \((v_1 - v_2)\) band: • measured values; — computation accounting for line-mixing; - - - - computation neglecting for line-mixing. Residuals (obs-calc) are given in the lower part.
Fig. 10. SAO radiance collected from 40 km for a tangent height of 15.8 km. The upper part gives measured values and the curves in lower part are measured-calculated deviations averaged over 0.1 cm$^{-1}$ obtained with (a) and without (b) inclusion of line mixing.

Fig. 2 can be compared with the results in Fig. 3 of Ref. [5]. It shows that discrepancies of our approach shows almost no broad structure under the local peaks (less than twice the uncertainty) whereas those obtained with the 12 codes in Ref. [5] all show significant broad errors (up to 10 and 20 times the uncertainty) between 670 and 780 cm$^{-1}$. Finally note that, in terms of brightness temperature, the discrepancies, whose local values reach 6 K, are all lower than 1.5 K when averaged over 1 cm$^{-1}$ with an RMS over the entire spectral range of 0.5 K (16, 8 and 1.3 K when the Voigt model is used). This demonstrates that our model brings a significant improvement in the problem of the calculation of the $v_2$ wings pointed out in [5].

Similar comparisons in the case of a ground-based measurement looking up are presented in Fig. 3. In this case, use of Voigt profiles leads to radiances that are significantly too strong due to the overestimation of the emission of low-altitude layers. Again, accounting for line-mixing with our model leads to a considerable improvement and discrepancies that only show local features on a flat background.

Analysis of the MIPAS spectra show that, for tangent altitudes $z_{tg}$ higher than about 50 km line-mixing has negligible influence on the spectra and can be neglected in forward calculations. Then, for $z_{tg}$ between 25 and 50 km, differences between calculations with and without the inclusion of line mixing are very localized and limited to Q branch wings as shown by the example given in
Fig. 4. Both models lead to very satisfactory results, except in the vicinity of the \((\nu_1 - \nu_2)\) Q branch near 720 cm\(^{-1}\) where the Voigt model fails (see Fig. 5) as already shown in Ref. [3]. This is due to the fact that the optical thickness in the wings, which depends on the squared pressure [2], is too small to make emission in the far wings significant for these lines of sight. As the tangent height decreases, the contribution of the wings increases rapidly and errors obtained with the Voigt model begin to spread over wider ranges as shown in Fig. 6. For lines of sight looking down deep into the atmosphere, the overestimation of radiances and the errors can be considerable as illustrated in Figs. 7 and 8. On the other hand, the approach proposed in [1] leads to satisfactory results although some significant discrepancies remain. The latter are partly due to uncertainties on the measurement and on some of the geophysical parameters along the optical path. There are also several other potential sources of error such as gain calibration, non-linearity correction, the possibly ice-coverage of the detector unit. However, since measurements available for this study were recorded in the commissioning phase and are based on preliminary processing parameters, it seems too early to explain these residuals in detail. Nevertheless, note the residual near 790 cm\(^{-1}\) that can be clearly seen in Fig. 8 and also appears in Figs. 6 and 7 whose reason is unexplained.

As analyzed in [3], when line-mixing effects are significant, use of the Voigt model can lead to underestimated, correct, or overestimated values of the emitted radiance in the wings. Indeed, this approach overestimates the emission of a given layer but underestimates the transmission of the atmosphere towards the observation point. The result then depends on the relative contributions of the various layers along the path. This is illustrated in Fig. 9 which gives a detailed view of the
results in the region near 750 cm\(^{-1}\). Errors obtained with the Voigt model on the emission in the troughs between the R lines of the \((\nu_1 - \nu_2)_1\) band are positive below 750 cm\(^{-1}\) and become negative above this point. This is due to competitive errors on the emission and transmission. Indeed, the overestimated emission by the \(\nu_2\) wings in low atmospheric layers is, below 750 cm\(^{-1}\) where R lines of the \((\nu_1 - \nu_2)_1\) band are strong, overabsorbed by higher layers leading to underestimated results. This underestimation of transmission then decreases when moving towards weaker lines at higher frequencies so that errors on radiance almost compensate near 750 cm\(^{-1}\) and become negative above.

Analysis of the SAO balloon-borne spectra again shows that, for tangent altitudes \(z_{tg}\) higher than about 25 km line-mixing significantly affects the near wing of intense Q branches only \([3]\). Comparisons between measured and calculated spectra for tangent altitudes between 10 and 16 km and calculated results are plotted in Figs. 10–12. They confirm the preceding conclusions concerning the quality of our model and the large errors obtained when Voigt line-shapes are used. Note that, as expected \([1]\), this is obtained in both the high- and low-frequency wings of the strong CO\(_2\) \(\nu_2\) band. The largest differences between predictions of our model and the measurements, which are observed near 730 cm\(^{-1}\), are due to a large absorption in the beam splitter that was used for this flight. Those and 760 and 800 cm\(^{-1}\) are Q branches of HNO\(_3\) and HCFC-22, species that were not accounted for in our calculations.

Nevertheless, most spectral regions where collected radiances are significant are correctly modeled although significantly influenced by line-mixing as shown in Fig. 13. Indeed, absorption in both
the low-frequency side of the \((v_1 - v_2)_{\|}\) band and high-frequency side of the \((v_1 - v_2)_{\perp}\) band are accurately calculated as shown in Fig. 13. Note that discrepancies near 588 cm\(^{-1}\) in Fig. 13a are due to our neglect of line-mixing effects in the \(v_2\) Q-branch of N\(_2\)O [15]. In some regions, the quality of the model proposed enables retrieval of species that lead to small emission highly contaminated by contributions of other molecules as shown in Fig. 14. Indeed, although surrounded and partly masked by intense CO\(_2\) lines [(\(v_1 - v_2\)\(_1\), \((v_1 + v_2 - v_1)\), and \((v_1 + v_2 - 2v_2)\) and Q lines of the \(v_1\) transition of O\(_3\), the contribution of the Q branch of the HNO\(_3\) \(v_8\) band is discernible and enables determination of the HNO\(_3\) amount (done here by scaling a standard profile) as shown by the plot.

6. Conclusion

The results presented in this paper have confirmed the quality of the line-mixing model proposed for CO\(_2\) in Ref. [1] and previously validated using laboratory measurements [1] as well as atmospheric transmissions [2]. This success opens interesting perspectives for the retrieval of \(P\) and \(T\) vertical profiles in the troposphere and lower stratosphere as well as for the analysis of species that make broad contribution to atmospheric spectra. Among these are heavy trace gases and aerosols but also clouds which are generally studied using wavenumbers of minimum atmospheric absorption.
Fig. 14. Radiances at 40 km for a tangent height of 9.8 km in the region of the ν8 Q branch of HNO3: • measured values; — computation accounting for line-mixing; Residuals (obs-calc) are given in the lower part where computations have been made with the Voigt model (a), our model without HNO3 (b), our model with HNO3 (c).

(e.g. [16,17] and those cited therein). A correct prediction of the “baseline” emission due to far wings contributions is then clearly essential. Finally, studying the impact of the present model on radiation budget calculations would also be of interest.

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